

UNIT FIVE

THERMODYNAMIC POTENTIALS AND PHASE TRANSITIONS

Introduction

We are familiar with five thermodynamic variables P, V, T, S and U. But according to first law of thermodynamics

$$dQ = dU + PdV$$

From the definition of entropy

$$dQ = TdS$$

$$TdS = dU + PdV$$

or

$$dU = TdS - PdV \quad \dots\dots (1)$$

This equation says that the fifth thermodynamic variable U is determined by P, V, T and S. This is the reason why only four thermodynamic variable are defined. Out of the four thermodynamic variables only two variable are required to describe the system completely. Taking two of the four thermodynamic variables P, V, T and S at a time there are six possible pairs. They are (P, V), (P, T), (P, S), (V, T), (V, S), and (T, S). The pairs (P, V) and (T, S) do not occur separately because in the basic equation (1) TdS forms one unit and PdV forms another and they do not occur separately. Thus we are left with four pairs of thermodynamic variables (P, T), (P, S), (V, T) and (V, S). Corresponding to each pair we can associate a function called thermodynamic function or thermodynamic potential. In equation (1) we can very well see that U is a function of (S, V). Similarly we have three more functions. The thermodynamic function associated with (T, V) pair is called Helmholtz function or free energy (A), that associated with the pair (S, P) is called enthalpy (H) and the function associated with the pair (T, P) is called Gibbs function (G).

Look at the functions carefully

$$(S, V), \quad (T, V), \quad (T, P), \quad (P, S)$$

I II III IV

Going from set I to set II only one variable is changed
Going from set II to set III only one variable is changed

Similarly going from III to IV again one variable is changed. This enables us go from I to II, II to III and III to IV by a mathematic technique called Legendre transformation.

Characteristic functions

Legendre transformation

If the state of the system is described by a function f of two variables (x, y)

i.e., $f = f(x, y)$

Taking differential on both sides

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad \dots (2)$$

Let $\frac{\partial f}{\partial x} = u$ and $\frac{\partial f}{\partial y} = v$

$$df = u dx + v dy \quad \dots (3)$$

\therefore Now we want to change the variables (x, y) to (u, y) . We get a new function $g(u, y)$ which can be expressed in terms of the differentials du and dy . Let g be a function of new variables u and y defined by the equation

$$g = f - ux \quad \dots (4)$$

Taking differential on both sides, we get

$$dg = df - u dx - x du$$

Putting the value of df , yields

$$dg = u dx + v dy - u dx - x du$$

or

$$dg = -x du + v dy \quad \dots (5)$$

which is exactly the desired form. From equation 5 we get

$$x = -\left(\frac{\partial g}{\partial u}\right)_y \quad v = \left(\frac{\partial g}{\partial y}\right)_x$$

Enthalpy (H)

We have

$$dU = -P dV + T dS$$

$$U = U(V, S)$$

we want to generate a function called enthalpy (H) which depends on (P, S) we make use of equation 4
i.e.

$$H = U - PV = U + PV$$

$$H = U + PV$$

Since U, P and V are state function enthalpy is also a state function.
From equation 6, we get

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

..... (7)

Thus H is obviously a function of (S, P)

Helmholtz function A

A is a function of (T, V) and U is function of (S, V). So we can go over from U to A by Legendre transformation using equation 4, we get

$$A = U - TS \quad \dots\dots (8)$$

Taking the differential

$$dA = dU - TdS - SdT$$

Substituting for dU, we get

$$dA = TdS - PdV - TdS - SdT$$

$$\text{or} \quad dA = -PdV - SdT \quad \dots\dots (9)$$

Thus A is obviously a function of (T, V).

Gibbs function G

G is a function of (P, T) and A is a function (V, T). This shows that we can go over from A to G by Legendre transformation. Using equation (4) we can define G.

$$G = A - PV$$

$$G = A + PV \quad \dots\dots (10)$$

Taking differentials on both sides, we get

$$dG = -PdV - SdT + PdV + VdP \quad \dots\dots (11)$$

$$dG = VdP - SdT$$

Thus G is obviously a function of P and T.

Altogether we obtained four differential equations that are formulations of first law of thermodynamics we collect all together

$$dU = -PdV + TdS \quad : \quad U(V, S)$$

$$dH = VdP + TdS \quad : \quad H(P, S)$$

$$dA = -PdV - SdT \quad : \quad A(V, T)$$

$$dG = VdP - SdT \quad : \quad G(P, T)$$

The main advantage of this formulation is that for example when a system undergoes changes in V and S then it is convenient to use differential equation for U . If P and T are convenient variables for describing a system we go for G . Similarly others.

The functions $U(V, S)$, $H(P, S)$, $A(V, T)$ and (G, P) are called thermodynamic potential functions. This is because they have the property that if functions are expressed in terms of appropriate thermodynamic variables, then all the thermodynamic properties of a system can be calculated by differentiation only.

Examples

(i) U is a function of V and S

$$\text{i.e.,} \quad U = U(V, S)$$

$$dU = \left(\frac{\partial U}{\partial V} \right)_S dV + \left(\frac{\partial U}{\partial S} \right)_V dS$$

we already have

$$dU = -PdV + TdS$$

comparing the two equations, we get

$$\left(\frac{\partial U}{\partial V} \right)_S = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S} \right)_V = T$$

(ii) H is a function of P and S

$$H = H(P, S)$$

$$dH = \left(\frac{\partial H}{\partial P} \right)_S dP + \left(\frac{\partial H}{\partial S} \right)_P dS$$

we have

$$dH = VdP + TdS$$

on comparing we get

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{and} \quad \left(\frac{\partial H}{\partial S}\right)_P = T$$

see also examples 2 and 3.

Example 1

Show that the Legendre transformation of $S(U, V)$ that produces the characteristic function $J\left(\frac{1}{T}, V\right)$ known as Massien function is given by the transform

$$J = -\frac{U}{T} + S = -\frac{A}{T}$$

$$dJ = \frac{U}{T^2} dT + \frac{P}{T} dV$$

and

Solution

$$S = S(U, V)$$

$$J = S - \frac{U}{T} \quad \dots\dots (1)$$

or

$$J = S - \frac{(A + TS)}{T} \quad A = U - TS$$

$$\therefore A = U - TS$$

$$J = -\frac{A}{T}$$

Taking differential on both sides of eq (1), we get

$$dJ = dS + \frac{U}{T^2} dT - \frac{1}{T} dU$$

Substituting for $dU = TdS - PdV$, we get

$$dJ = dS + \frac{U}{T^2} dT - \frac{TdS}{T} + \frac{PdV}{T}$$

or

$$dJ = \frac{U}{T^2} dT + \frac{PdV}{T}$$

Example 2

Show that $\left(\frac{\partial A}{\partial V}\right)_T = -P$ and $\left(\frac{\partial A}{\partial T}\right)_V = -S$

Solution

We know that $A = A(V, T)$. Taking differentials on both sides, yields

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

we have the relation

$$dA = -PdV - SdT$$

on comparing we get

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S.$$

Example 3

Show that $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$

Solution

We know that $G = G(P, T)$

Taking differentials on both sides, we get

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

We have the relation

$$dG = VdP - SdT$$

on comparing we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Example 4

Derive the relation $U = A - T\left(\frac{\partial A}{\partial T}\right)_V$

Solution
We have
Using

$$= -T^2 \left(\frac{\partial(A/T)}{\partial T} \right)_V$$

$$U = A + TS$$

..... (1)

$$\left(\frac{\partial A}{\partial T} \right)_S = -S$$

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_V$$

$$\left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_V = -A \cdot \frac{1}{T^2} + \frac{1}{T} \left(\frac{\partial A}{\partial T} \right)_V$$

or

$$T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_V = -A + T \left(\frac{\partial A}{\partial T} \right)_V$$

or

$$-T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_V = A - T \left(\frac{\partial A}{\partial T} \right)_V = A + TS = U.$$

Example 5

Show that

$$C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)$$

Solution

We have $U = A + TS$

Differentiate with respect to T , keeping V constant

$$\left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial A}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial T} \right)_V + S$$

or

$$\left(\frac{\partial U}{\partial T} \right)_V = -S + T \left(\frac{\partial S}{\partial T} \right)_V + S$$

Use

$$\left(\frac{\partial U}{\partial T} \right)_V = C_V$$

Using

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

∴

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

$$C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_V$$

Enthalpy-Joule-Thomson expansion or Throttling process

The throttling process is also known as a porous plug process or a Joule - Thomson expansion. To understand this process consider a cylinder thermally insulated and provided with two adiabatic pistons on opposite sides of a porous wall which is also adiabatic (see figure below). The porous wall allows the gas (system) to flow from one side to another while changing pressure. Between the left hand side piston and the porous wall there is a gas at pressure P_1 and volume V_1 . Since the right hand piston against the wall prevents any gas from seeping through the porous plug, the initial state of the gas is an equilibrium state contained between the two pistons. Now imagine that both pistons move simultaneously at different speeds to the right such that a constant higher pressure P_1 is maintained on the left hand side of the porous wall and a constant lower pressure P_2 is maintained on the right hand side. After all the gas flowed through the porous plug, the final equilibrium state of the system is reached (see figure 5.1). This is called a throttling process or a Joule-Thomson expansion.

This throttling process is an irreversible process due to friction between the gas and the walls of the pores in the plug. In other words, the gas passes through dissipative non-equilibrium states

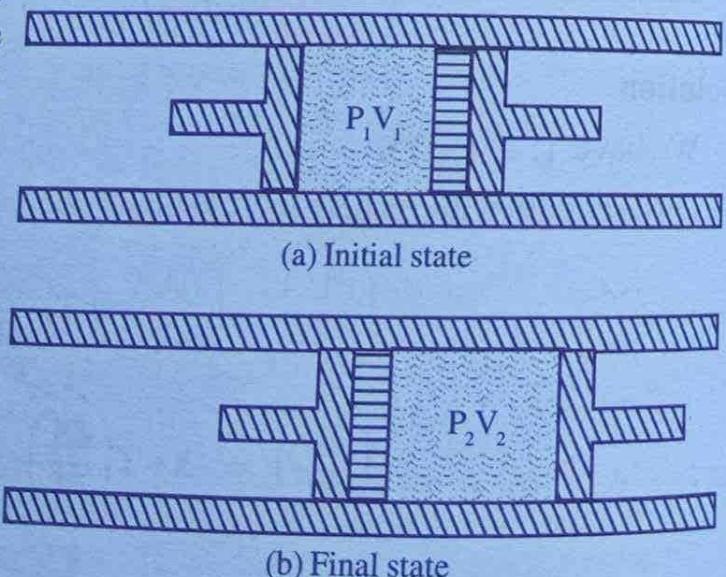


Figure 5.1

on its way from initial equilibrium state to the final equilibrium state. These intermediate non-equilibrium states cannot be described by thermodynamic coordinates, but an interesting conclusion can be drawn about the initial and final equilibrium states, which are described by the thermodynamic coordinates.

From the first law we have

$$dU = dQ + dW$$

$$U_2 - U_1 = Q - \int PdV \quad \therefore dW = PdV$$

or

Since the throttling process occurs in an adiabatic enclosure $Q = 0$, we get

$$U_2 - U_1 = - \int PdV \quad \dots\dots (12)$$

The right hand side is the work done on the system.

$$-\int PdV = - \int_{V_1}^0 P_1 dV - \int_0^{V_2} P_2 dV$$

$$-\int PdV = +P_1 V_1 - P_2 V_2$$

Now equation 12 becomes

$$U_2 - U_1 = +P_1 V_1 - P_2 V_2$$

or

$$U_2 + P_2 V_2 = U_1 + P_1 V_1$$

$$H_2 = H_1 \quad \dots\dots (13)$$

Note: It is not correct to say that enthalpy remains constant during a throttling process since it is an irreversible process and passing through non-equilibrium states and we cannot predict what is happening in the intermediate states.

Other properties of enthalpy

1. We have

$$dH = TdS + VdP \quad \dots\dots (14)$$

or

$$dH = dQ + VdP$$

Dividing throughout by dT , we get

$$\frac{dH}{dT} = \frac{dQ}{dT} + \frac{VdP}{dT}$$

At constant pressure

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{dQ}{dT}\right)_P$$

By definition $\left(\frac{dQ}{dT}\right)_P = C_P$

i.e., $\left(\frac{\partial H}{\partial T}\right)_P = C_P \quad \dots\dots (15)$

Equation 14 shows that the function enthalpy H is related to an experimental quantity the specific heat capacity at constant pressure. This equation provides a means of calculating the enthalpy from C_P .

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

or $H_2 - H_1 = \int_1^2 C_P dT \quad \dots\dots (16)$

For an ideal gas C_P is a constant, thus

$$H_2 - H_1 = C_P(T_2 - T_1)$$

2. For an isobaric process, equation 14 becomes

$$dH = TdS$$

or $dH = dQ$

i.e., $H_2 - H_1 = Q_P \quad \dots\dots (17)$

This shows that the change in enthalpy during an isobaric process is equal to the heat that is transferred between the system and the surroundings.

3. For an adiabatic process, equation 14 becomes

$$dH = VdP \quad \text{integrating}$$

$$H_2 - H_1 = \int_1^2 VdP \quad \dots\dots (18)$$

R.H.S is the area under the curve of PV diagram projected to the pressure axis.
 In an $x - y$ graph we can have two areas under the curve one is $-\int y dx$ and the other one is $\int x dy$. $-\int y dx$ is the area under the curve projected on to x-axis and $\int x dy$ is the area of the curve projected onto the y-axis as shown in figure below.

Similarly in PV diagram the area under the curve which give work done are of two type 1) $-\int P dV$ 2) $\int V dP$. See figure below.

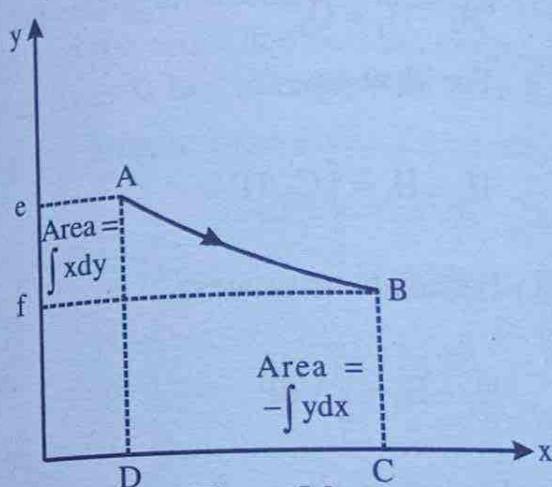


Figure 5.2

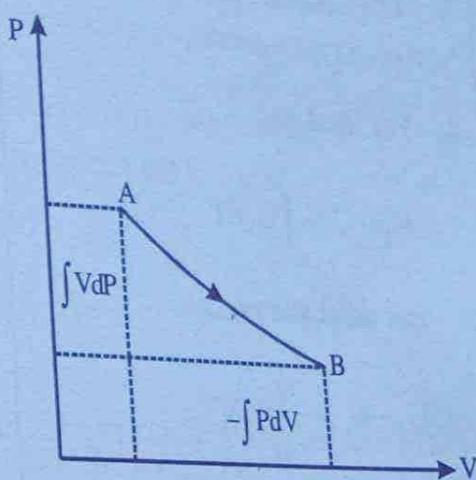


Figure 5.3

Note: $-\int P dV$ is the adiabatic work and $\int V dP$ is the flow work.

- For a reversible isobaric-adiabatic process equation 14 becomes

$$dH = 0$$

or

$$H = \text{constant}$$

Thus enthalpy is defined as that something which remains constant during a reversible isobaric-adiabatic process.

Comparison of properties of U and H of a hydrostatic system

Internal energy U(V, S)

1. For free expansion (irreversible)

$$H_f = H_i$$

$$2. \quad dU = dQ - PdV$$

$$\left(\frac{\partial U}{\partial T} \right)_V = C_V$$

3. For isochoric process

$$U_f - U_i = Q_V$$

4. For ideal gas

$$U_f - U_i = \int_i^f C_V dT$$

5. For adiabatic process

$$U_f - U_i = - \int_i^f P dV$$

6. For infinitesimal change

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial S} \right)_V = T$$

$$\left(\frac{\partial U}{\partial V} \right)_S = -P$$

Enthalpy H (P, S)

1. Throttling process (irreversible)

$$H_f = H_i$$

$$2. \quad dH = dQ + VdP$$

$$\left(\frac{\partial H}{\partial T} \right)_P = C_P$$

3. For isobaric process

$$H_f - H_i = Q_P$$

4. For ideal gas

$$H_f - H_i = \int_i^f C_P dT$$

5. For adiabatic process

$$H_f - H_i = \int_i^f VdP$$

6. For infinitesimal change

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T$$

$$\left(\frac{\partial H}{\partial P} \right)_S = V$$

Helmholtz and Gibbs functions

Helmholtz function and its properties

1. The Helmholtz function A(T, V) was defined as

$$A = U - TS \quad \dots \dots (19)$$

For any infinitesimal reversible process

$$dA = -PdV - SdT$$

..... (20)

The pressure and entropy can be calculated from partial differential equations.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S$$

For a reversible isothermal process $dT = 0$

$$dA = -PdV$$

$$A_f - A_i = - \int_i^f PdV \quad \dots \dots (21)$$

or

It means that an increase in Helmholtz function during an isothermal process is equal to the work done on the system. For this reason Helmholtz function is referred to as free energy of the system at constant temperature.

For any infinitesimal isothermal process equation (19) becomes

$$(\Delta A)_T = (\Delta U)_T - T(\Delta S)_T$$

or

$$(\Delta A)_T = (\Delta U)_T - (\Delta Q)_T$$

i.e.

$$(\Delta A)_T = (\Delta W)_T$$

This means that the decrease of the Helmholtz energy $(\Delta A)_T$ of the system equals the maximum amount of isothermal work $(\Delta W)_T$ that is performed by the system. The internal energy of the system also decreases. But this is not equal to $(\Delta W)_T$ since

$$(\Delta U)_T - (\Delta Q)_T = (\Delta W)_T$$

as

$$(\Delta Q)_T \geq 0$$

$$(\Delta W)_T \leq (\Delta U)_T$$

3. For a reversible isothermal-isochoric process, equation 20 gives

$$dA = 0$$

or

$$A = \text{constant}$$

i.e. Helmholtz function of a system remains constant during reversible isothermal-isochoric process.

4. When a system is in equilibrium it tries to minimise its internal energy and tries to maximise its entropy. Thus $A = U - TS$, the Helmholtz function is always minimum for a system in equilibrium.

Properties of Gibbs function

1. The Gibbs function $G(T, P)$ was defined to be

$$\begin{aligned} G &= A + PV \\ \text{or} \quad G &= U - TS + PV & (\because A = U - TS) \\ \text{or} \quad G &= H - TS & (\because H = U + PV) \end{aligned}$$

For any infinitesimal reversible process we have

$$dG = VdP - SdT \quad \dots\dots (22)$$

The entropy and volume can be calculated by the partial differential equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

2. If the process is reversible isothermal and isobaric $dT = 0$ and $dP = 0$, equation (22) gives

$$dG = 0$$

$$G = \text{constant}$$

i.e., during a reversible isothermal and isobaric process Gibbs function remains constant. For example first order change of phase. The processes like sublimation, fusion and vapourisation takes place at constant temperature and pressure. Hence during such processes the Gibbs function of the system remains constant.

Maxwell's thermodynamical relations

Maxwell established four relations between the four thermodynamic quantities P, V, T and S . There are several methods to derive these relations. We adopt here the method based on the four thermodynamic potentials U, H, F and G . By using the condition for an exact differential we can derive Maxwell's relations. This is possible since dU, dH, dF and dG are exact differentials. You may think that how do we say that they are exact differentials. Suppose we go from a point A to point B and come back to A in a $P-V$ diagram where all the points are uniquely fixed. The net changes in the values of P, V, T, S and U are all zero.

i.e. $\oint dP = 0, \oint dV = 0, \oint dT = 0, \oint dS = 0 \text{ and } \oint dU = 0.$

Therefore dP, dV, dT, dS and dU are exact differentials.

The differentials of any quantity which depends on P, V, T, S, U etc. (e.g. $TS, PV, U + TS, U + PV$ etc.) will also be a perfect differential. It follows that dU, dF, dH and dG are all exact differentials.

Condition for exact differential

If a relation exists among x, y and z , then we suppose that z is a function of x and y .

i.e. $z = z(x, y)$

Taking the differentials on both sides we get

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

Put $M = \left(\frac{\partial z}{\partial x} \right)_y \text{ and } N = \left(\frac{\partial z}{\partial y} \right)_x$

then $dz = Mdx + Ndy$

where z, M and N are functions of x and y . Partially differentiating M with respect to y and N with respect to x , we get

$$\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{\partial y \partial x}$$

and $\left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{\partial x \partial y}$

since the second derivatives of the right hand terms are equal, it follows that

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad \dots \dots (23)$$

This is the condition for exact differential

Maxwell's relations

(i) From first law we have

$$dU = TdS - PdV$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get $M = T$, $N = -P$, $x = S$, $y = V$ and $z = U$

$$\text{But } M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y} \right)_x$$

$$\text{or } T = \left(\frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad -P = \left(\frac{\partial U}{\partial V} \right)_S$$

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

$$\text{We get } \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \dots \dots (24)$$

This is the first Maxwell's relation.

(ii) From the enthalpy change, we have

$$dH = TdS + VdP$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get $z = H$, $M = T$, $x = S$, $N = V$ and $y = P$

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

$$\text{We get } \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad \dots \dots (25)$$

This is the second Maxwell's relation

(iii) From the Helmholtz function change, we have

$$dF = -SdT - PdV$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get $z = F$, $M = -S$, $x = T$, $N = -P$ and $y = V$.

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

We get $-\left(\frac{\partial S}{\partial V} \right)_T = -\left(\frac{\partial P}{\partial T} \right)_V$

or $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \dots\dots (26)$

This is the third Maxwell's relation.

(iv) From the Gibbs function change, we have

$$dG = -SdT + VdP$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get

$$z = G, M = -S, x = T, N = V \text{ and } y = P$$

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

or $\left(\frac{\partial S}{\partial P} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_P \dots\dots (27)$

This is the fourth Maxwell's relation.

Equations 24, 25, 26 and 27 are called Maxwell's thermodynamic relations.

A device to remember four characteristic functions and their relations

To deal with characteristic functions U, A, H and G it is necessary to remember their functional dependence, all of its partial derivatives leading to thermodynamic variables and Maxwell's relations. It is not possible to memorise all these 16 ($4 + 8 + 4$) relations. For this we devised a mnemonic diagram called VAT - VUS diagram. VAT - VUS diagram is a square labelled the corners with V, A, T and V, U, S as shown.

The fourth unlabelled corner of the square is labelled with the remaining fourth thermodynamic variable P. Thermodynamic functions are marked on the sides of the square. We have to fill two more thermodynamic functions G and H. Fill it with alphabetic order starting from A. After A, G comes first and then H. Fill it accordingly. Finally draw arrow marks from S and P to its conjugate variables T and V respectively. Now VAT-VUS diagram becomes figure 5.5.

This diagram containing all 16 relations that we require.

For example A is in between V and T. This implies that A is a function of V and T. Similarly U is a function of V and S, G is a function of T and P and H is a function of S and P once functional dependence is known, the differential of the thermodynamic function is always equal to the sum of the terms that include the differential of the thermodynamic coordinates. The coefficient of the differential in each term is found by connecting the arrow from the thermodynamic coordinate of the differential to its conjugate coordinate.

Example 1

$$A = A(V, T)$$

$$dA = (\) dV + (\) dT$$

$$\left(\frac{\partial A}{\partial V} \right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T} \right)_V = -S$$

In both cases connection goes against the arrow mark.

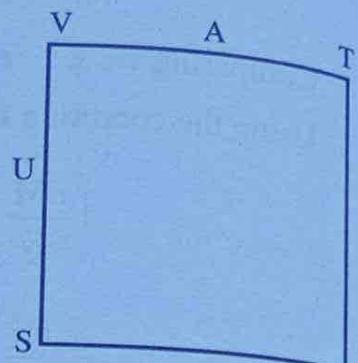


Figure 5.4

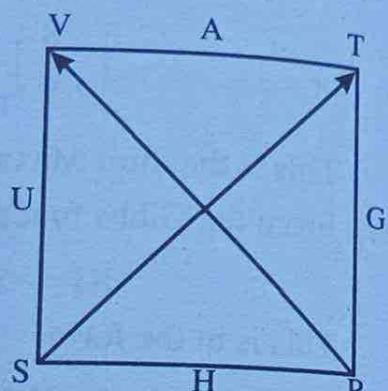


Figure 5.5

Example 2

$$U = U(V, S)$$

$$dU = (\) dV + (\) dS$$

$$\left(\frac{\partial A}{\partial V} \right)_T = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S} \right)_V = T$$

$$\therefore dU = -PdV + TdS$$

Example 3

$$G = G(T, P)$$

$$dG = (\) dT + (\) dP$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P} \right)_T = V$$

$$\text{Thus} \quad dG = -SdT + VdP$$

Example 4

$$H = H(S, P)$$

$$dH = (\) dS + (\) dP$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P} \right)_S = V$$

$$\therefore dH = TdS + VdP$$

Finally we can write down all four Maxwell's relations from the VAT-VUS diagram by applying the condition for exact differential

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

It is better you to construct your own gimmick by closely observing Maxwell's relations and the diagram.

TdS equations

The entropy of a pure substance can be considered as a function of two variables such as T and V. Thus

i.e.

$$S = S(T, V)$$

$$\therefore dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

Multiplying throughout by T , we get

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\text{But } T \left(\frac{\partial S}{\partial T} \right)_V = C_V$$

From Maxwell's relations, we have

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\therefore TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

This is called first TdS equation.

Second TdS equation

The entropy of a pure substance can be considered as a function of two variables T and P .

i.e.

$$S = S(T, P)$$

$$\therefore dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

or

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP$$

But $T \left(\frac{\partial S}{\partial T} \right)_P = C_P$ and from Maxwell's relations

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

∴ We get

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

This is called the second TdS equation.

Variation of intrinsic energy with volume

When a system undergoes an infinitesimal reversible process between two equilibrium states, the change in intrinsic energy is given by

$$dU = dQ - PdV$$

or

$$dU = TdS - PdV.$$

Substituting for TdS from first TdS equation, we get

$$dU = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_v dV - PdV$$

But from $U = U(T, V)$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Comparing this equation with the above equation

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

This is the energy equation of state. From this the change in energy (dU) can be calculated.

Case I Perfect gas

Consider one mole of perfect gas, we have

$$PV = RT$$

$$\therefore P = \frac{RT}{V}$$

$$\text{or } \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$$

From the energy equation, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{R}{V} - P$$

or $\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \quad \left(\because \frac{RT}{V} = P\right)$

It means that there is no change in the intrinsic energy of a perfect gas during an isothermal change in volume. (see also example 1).

Case II Real gas

For one mole of gas, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P + \frac{a}{V^2} = \frac{RT}{V - b}$$

$$\therefore P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

From the energy equation, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

or $\left(\frac{\partial U}{\partial V}\right)_T = \frac{TR}{V - b} - P = \frac{a}{V^2}$

We also have

$$dU = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV - P dV = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dP$$

$$dU = C_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$dU = C_v dT + \frac{a}{V^2} dV$$

Integrating we get

$$U = \int C_v dT - \frac{a}{V} + \text{constant}$$

This shows that the intrinsic energy of an actual gas increases with isothermal increase in volume.

Applications of TdS equations

- Suppose a system undergoes a reversible isothermal change of pressure. Here our aim is to calculate the amount of heat transferred, the work done and the change in internal energy of the system.

For this consider the second TdS equation.

Thus $TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$

For isothermal process $dT = 0$

Thus $TdS = -T \left(\frac{\partial V}{\partial T} \right)_P dP$

or $dQ = -T \left(\frac{\partial V}{\partial T} \right)_P dP$

From the definition of volume expansivity

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

or $\left(\frac{\partial V}{\partial T} \right)_P = \beta V$

∴ $dQ = -T\beta V dP$

Integrating, we get

$$Q = -T \int_{P_i}^{P_f} \beta V dP$$

Where P_i is the initial pressure and P_f is the final pressure.
In the case of solids and liquids β and V are almost constants.

This
$$Q = -TV\beta \int_{P_i}^{P_f} dP$$

$$Q = -TV\beta(P_f - P_i)$$

(see example 6 and 7)

This is the expression for heat transferred in a reversible isothermal pressure change.

Now we calculate the work done.

Work done,
$$W = - \int P dV$$

At constant temperature, dV can be written as

$$dV = - \left(\frac{\partial V}{\partial P} \right)_T dP$$

$$\therefore W = - \int P \left(\frac{\partial V}{\partial P} \right)_T dP$$

From the definition of isothermal compressibility

$$k = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

or
$$\left(\frac{\partial V}{\partial P} \right)_T = -kV$$

$$W = \int_{P_i}^{P_f} kVP dP$$

since K and V are almost constants take it outside the integral, then integrate we get

$$W = \frac{kV}{2} (P_f^2 - P_i^2)$$

This is the expression for work done. (See example 10(b))

From Q and W, we can very well calculate the internal energy U, by using first law of thermodynamics.

i.e. $\Delta W = Q + W$ (See example 10)

2. Suppose a system undergoes a reversible adiabatic change of pressure
From second TdS equation, we have

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dP$$

For adiabatic process $dS = 0$

$$0 = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dP$$

or $dT = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_p dP$

From $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

or $\left(\frac{\partial V}{\partial T} \right)_p = \beta V$

$\therefore dT = \frac{T}{C_p} V \beta dP$

Integrating we get

$$\Delta T = \int_{P_i}^{P_f} \frac{T}{C_p} V \beta dP$$

Suppose pressure increases, obviously β is positive. Since T, V, β and C_p are constants.

$$\Delta T = \frac{TV\beta}{C_p} (P_f - P_i) \quad \dots\dots (1)$$

This is the expression for the change in temperature when a system undergoes a reverse adiabatic change of pressure. This can be applied to all solids and liquids. (See example 10)

Example 6

One mole of van der waals gas undergoes a reversible isothermal expansion from volume V_1 to V_2 . Calculate the amount of heat transferred.

Solution

From first TdS equation we have

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_v dV$$

From van der waals equation, we have

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b}$$

$$\text{Hence } TdS = C_v dT + \frac{TR}{V-b} dV$$

For isothermal expansion $dT = 0$

$$TdS = \frac{TR}{V-b} dV$$

or $dQ = \frac{TR}{V-b} dV$ integrating

$$Q = TR \ln(V-b) \Big|_{V_1}^{V_2}$$

So

$$Q = RT \ln \left(\frac{V_2 - b}{V_1 - b} \right)$$

Example 7

If the pressure on 15 cm^3 of mercury at 20°C is increased reversibly and isothermally from 0 to 1000 atm; calculate the heat transferred. $\beta = 1.81 \times 10^{-4} \text{ K}^{-1}$, $1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$

Solution

From the second TdS equation, we have

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dP$$

For isothermal process $dT = 0$

$$dQ = -T \left(\frac{\partial V}{\partial T} \right)_p dP$$

Integrating we get

$$Q = -T \int_0^{1000} \left(\frac{\partial V}{\partial T} \right)_p dP$$

But $\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \beta \quad \text{or} \quad \left(\frac{\partial V}{\partial T} \right)_p = \beta V$

$$\therefore Q = -T \int_0^{1000} \beta V dP$$

For solid β and V are almost constants.

$$Q \approx -T\beta V \times (1000 \text{ atm})$$

$$Q \approx -293 \times 1.81 \times 10^{-4} \times 1.5 \times 10^{-5} \times 1000 \times 1.01 \times 10^5$$

$$Q \approx -80.34 \text{ J}$$

Note: TdS equations are very useful to calculate the heat transferred, the change in temperature and change in pressure.

Example 8

Derive the third TdS equation

$$TdS = C_v \left(\frac{\partial T}{\partial P} \right)_V dP + C_p \left(\frac{\partial T}{\partial V} \right)_P dV$$

Solution

Assume that entropy is a function of P and V.

i.e.

$$S = S(P, V)$$

\therefore

$$dS = \left(\frac{\partial S}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial V} \right)_P dV$$

or

$$TdS = T \left(\frac{\partial S}{\partial P} \right)_V dP + T \left(\frac{\partial S}{\partial V} \right)_P dV$$

$$\left(\frac{\partial S}{\partial P} \right)_V = \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_V$$

$$\left(\frac{\partial S}{\partial V} \right)_P = \left(\frac{\partial S}{\partial T} \right)_P \left(\frac{\partial T}{\partial V} \right)_P$$

$$\therefore TdS = T \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_V dP + T \left(\frac{\partial S}{\partial T} \right)_P \left(\frac{\partial T}{\partial V} \right)_P dV$$

$$\text{But } T \left(\frac{\partial S}{\partial T} \right)_V = C_V \quad \text{and} \quad T \left(\frac{\partial S}{\partial T} \right)_P = C_P$$

$$\therefore TdS = C_V \left(\frac{\partial T}{\partial P} \right)_V dP + C_P \left(\frac{\partial T}{\partial V} \right)_P dV$$

Example 9

Show that first TdS equation may be written as

$$TdS = C_V dT + \frac{\beta}{k} T dV$$

Solution

From first TdS equation we have

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \quad \dots\dots (1)$$

Using

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad k = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\therefore \frac{\beta}{k} = -\frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial P} \right)_T} = -\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

Put this in equation (1) yields

$$TdS = C_V dT + T \frac{\beta}{k} dV.$$

Example 10

The pressure on 500 g of copper is increased reversibly and isothermally from 0 to 5000 atm at 298K($\rho = 8.96 \times 10^3 \text{ kg m}^{-3}$), volume expansivity $\beta = 49.5 \times 10^{-6} \text{ K}^{-1}$, isothermal compressibility $k = 6.18 \times 10^{-12} \text{ Pa}^{-1}$ and specific heat $C_p = 385 \text{ J kg}^{-1} \text{ K}$ to be constant.

- How much heat is transferred during the compression?
- How much work is done during compression?
- Determine the change of internal energy.

Solution

$$m = 0.5 \text{ kg}, \quad T = 298 \text{ K}, \quad \beta = 49.5 \times 10^{-6} \text{ K}^{-1}, \quad k = 6.18 \times 10^{-12} \text{ Pa}^{-1}$$

$$C_p = 385 \text{ J kg K}^{-1}.$$

- Heat transferred $Q = TV\beta P_f$ (see example 7)

$$Q = -298 \times \frac{0.5}{8.96 \times 10^3} \times 49.5 \times 10^{-6} \times 5000 \times 1.01 \times 10^5$$

$$Q = -298 \times 5.58 \times 10^{-5} \times 49.5 \times 10^{-6} \times 5 \times 1.01 \times 10^8$$

$$Q = -298 \times 5.58 \times 4.95 \times 5 \times 1.01 \times 10^{-2}$$

$$Q = -415.67 \text{ J}$$

b) Work done,

$$W = \frac{1}{2} kV(P_t^2 - P_i^2)$$

$$W = \frac{6.18 \times 10^{-12}}{2} \times \frac{0.5}{8.96 \times 10^3} (5000 \times 1.01 \times 10^5)^2$$

$$W = 43.97 \text{ J}$$

c)

$$\Delta U = \Delta Q + \Delta W$$

$$\Delta U = -415.67 + 43.97$$

$$\Delta U = -371.7 \text{ J}$$

Example 11

From the Maxwell's equation show that for a perfect gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Solution

We have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

or

$$\frac{1}{T} \left(\frac{\partial Q}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

or

$$\left(\frac{\partial Q}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

But

$$\delta Q = dU + PdV$$

∴

$$\frac{dU + PdV}{dV} = T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{dU}{dV} + P = T \left(\frac{\partial P}{\partial T}\right)_V$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

For a perfect gas $PV = RT$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{PV}{V} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

Example 12

Using Maxwell's relation show that $C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$. Deduce

$C_P - C_V = R$ for a perfect gas.

Solution

We have $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying throughout by T , we get

$$T \left(\frac{\partial S}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

By definition

$$T \left(\frac{\partial S}{\partial T}\right)_P = C_P$$

and

$$T \left(\frac{\partial S}{\partial T}\right)_V = C_V$$

$$C_p = C_v + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

or

$$C_p - C_v = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

From Maxwell's relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$

$$\therefore C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

For a perfect gas $PV = RT$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$$

and

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\therefore C_p - C_v = T \frac{R}{V} \frac{R}{P} = \frac{TR^2}{RT}$$

$$\therefore C_p - C_v = R$$

Example 13

Prove that $\left(\frac{\partial C_v}{\partial V} \right)_T = 0$ for an ideal gas as well as for a Vander waal's gas. What does it mean.

Solution

We have

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \text{ (see example 3)}$$

For an ideal gas

$$PV = RT$$

or

$$P = \frac{RT}{V}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$$

and

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_V = 0$$

$$\left(\frac{\partial C_V}{\partial V} \right)_T = 0$$

This means that at a given temperature C_V is independent of volume

For a vander waals gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2} \right)_V = 0$$

$$\therefore \left(\frac{\partial C_V}{\partial V} \right)_T = 0$$

This means that at a given temperature C_V is independent of volume.

Example 14

Show that the differential of the thermodynamic potential U may be written as

$$dU = (C_p - PV\beta)dT + V(kP - \beta T)dP$$

Solution

We have

$$dU = TdS - PdV \quad \dots\dots (1)$$

of

$$V = V(P, T)$$

then

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT$$

$$S = S(P, T)$$

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT$$

Put this in eqn (1), we get

$$dU = \left[T \left(\frac{\partial S}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[T \left(\frac{\partial S}{\partial P} \right)_T - P \left(\frac{\partial V}{\partial P} \right)_T \right] dP$$

$$T \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial Q}{\partial T} \right)_P = C_P.$$

By definition

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \beta V$$

$$\therefore dU = (C_P - P\beta V) dT + \left[T \left(\frac{\partial S}{\partial P} \right)_T - P \left(\frac{\partial V}{\partial P} \right)_T \right] dP$$

$$\text{By definition } k = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\left(\frac{\partial V}{\partial P} \right)_T = -kV$$

From Maxwell's relation

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -\beta V$$

$$\therefore dU = (C_P - P\beta V) dT + (kP - \beta T) V dP.$$

Example 15

Derive the relation $\left(\frac{\partial P}{\partial T} \right)_S = \frac{C_P}{V\beta T}$

Solution

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Substituting C_p and β on the R.H.S. of the given equation, we get

$$\text{R.H.S.} = \frac{T \left(\frac{\partial S}{\partial T} \right)_P}{V \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_B T} = \frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial T} \right)_P}$$

$$\text{R.H.S.} = \left(\frac{\partial S}{\partial V} \right)_P = \left(\frac{\partial P}{\partial T} \right)_S \quad (\text{By Maxwell's relation})$$

= L.H.S.

PV diagram for a pure substance

To draw a PV diagram for a pure substance we need a set of values of P and V. To obtain this we conduct a simple experiment. Here we take pure water as the pure substance since the triple point water is the bases of the thermodynamic temperature scale.

The experimental arrangement consists of a graduated cylinder 2 litres in volume closed at one end and the other end is provided with a piston. The pressure inside the cylinder is measured by a manometer and the temperature inside is controlled by ovens and refrigerators. Initially the cylinder is evacuated.

To begin the experiment 1 gram of water at 94°C introduced into the cylinder. It is due to vacuum inside, water will evaporate completely. Now the cylinder is filled with unsaturated vapour. This unsaturated vapour state of the system is represented by the point A on the system. The pressure of vapour is read from the manometer this will be obviously less than the atmospheric pressure.

Slowly compress the piston isothermally, volume of vapour decreases and pressure increases until the system reaches a state of saturated vapour. This state is represented by the point B on the PV diagram.

If the compression is continued condensation occurs to form water droplets. During compression pressure remains constant as long as the temperature is constant and volume decreases. The region BC represents the change of the system from vapour state to liquid state i.e. liquefaction. In this region vapour and liquid are in equilibrium. This is represented by the straight line BC on the PV diagram. The

constant pressure at which isothermal isobaric condensation occurs is called the vapour pressure. The line CB represents the isothermal isobaric evaporation of water vapour. Here the volume increases. The line BC or CB are called vapourisation line. At any point between B and C water and vapour coexist in equilibrium. At the point C, the system is only liquid water or saturated liquid.

Suppose we want to compress liquid water slightly a very large increase of pressure is required. It is represented by the vertical line CD on the PV diagram.

It may be noted that any point on the line AB is in the vapour state, any point on the line BC, there is equilibrium between vapour and liquid phases. The curve ABCD is a typical isotherm with discontinuities at B and C.

A graph is plotted between P and V at various temperatures called isotherms.

If we increase the temperature and drawing isotherms, it can be seen that the vapourisation line (horizontal line) becomes shorter. As the temperature rises ultimately the vapourisation line vanishes. **The temperature at which the vapourisation line vanishes is called critical temperature (T_c)**. The corresponding volume and pressure are called critical volume (V_c) and critical pressure (P_c) respectively. It is seen that the critical point (point corresponding to P_c and V_c on the isotherm) is a point of inflection on the PV diagram. The isotherm at the critical temperature is called the critical isotherm. (see the PV diagram).

Results of the experiment

1. For every substance, there is a critical temperature characteristic of the substance.
2. Above the critical point the isotherms are continuous curves which lose their inflection points and take the form of rectangular hyperbolas.
3. Above the critical point there is no longer any distinction between a liquid and a vapour. That is meniscus between the liquid and vapour disappears.

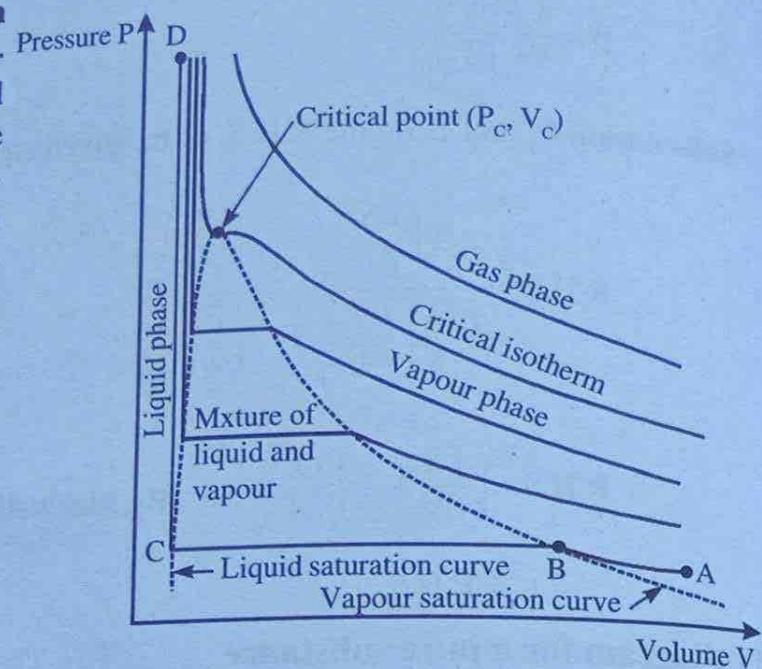


Figure 5.6: Isotherms of pure substance water

4. At critical temperature the densities of the vapour and liquid are the same.

If the densities of both liquid and vapour of water are measured as functions of temperature and a graph is plotted between temperature and density we get a graph as shown in figure 5.7. From the graph we can evaluate the critical temperature, where density of liquid is equal to density of water. The graph also gives critical density. At temperatures below the critical point the liquid and vapour densities vary only slightly and are significantly different from each other.

For H_2O the critical temperature is 647.067K and critical pressure is 22.046MPa and critical volume for 1kg is 0.00309 m^3 and the critical density is 322.778 kg/m^3 .

If the pure substance is a solid we have a solid phase and a solid-vapour phase. It occurs in the low-temperature region than the liquid-vapour phase. This is not shown in our graph.

In the solid-vapour of the PV diagram, the isotherms have the same general character as the vapourisation lines in the liquid-vapour region. This horizontal line represents the isobaric transition from solid to vapour or sublimation. There is one such line that separates the solid-vapour region below from the liquid-vapour region above. The line is associated with the co-existence of all the three phases together called the triple point. Its value for water is 273.16K.

When a liquid or solid is in equilibrium with vapour at a given temperature, the vapour exerts a pressure that depends only on the temperature. In general, the higher the temperature the greater the vapour pressure. As the temperature of a liquid is lowered at triple point the liquid starts to solidify. At lower temperatures only solid and vapour are present. The vapour pressure of most solids is very small.

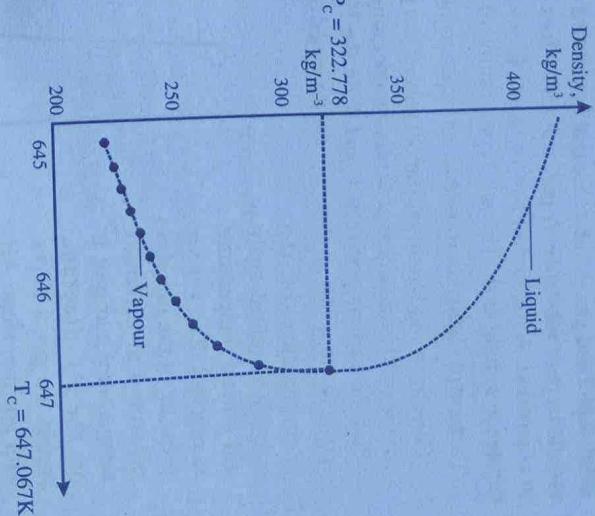


Figure 5.7: Density curves of liquid and vapour

PT diagram for a pure substance: phase diagram

A graph showing the variation of pressure with temperature is called PT diagram. A PT diagram is the most common way to show the phases of a pure substance hence called as phase diagram. At its simplest a phase can be just another term for solid, liquid and gas. A substance that has a fixed chemical composition throughout is called a pure substance. A pure substance does not have to be of a single element or compound. A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.

To draw phase diagram conduct an experiment in the following way.

1. Consider a solid (pure substance) at very low temperature. The vapour pressure of the solid is measured at various temperatures until the triple point is reached. Plot the various points of P and T on the PT diagram. We get a curve with positive slope OA as shown in figure called sublimation curve.

2. Temperature of the

sample is raised again Pressure P till critical temperature is reached. The vapour pressure of the liquid is measured at different temperature and plot it on the PT diagram. Again we get a curve with positive slope AB as shown in figure 5.8 called vapourisation curve.

The graph so obtained is called a phase diagram.

3. If a substance at its triple

point is compressed until there is no vapour left and the pressure on the resulting mixture of solid and liquid is increased, the temperature must change for equilibrium to exist between the solid and the liquid. Measure the pressures and temperatures of the solid coexisting with the liquid. Plot it on the same PT diagram. We get a curve with positive or negative AC as shown in slope figure above is called fusion curve. This is the picture of complete phase diagram of a pure substance.

It may be noted that (i) the sublimation curve represents the coexistence of solid

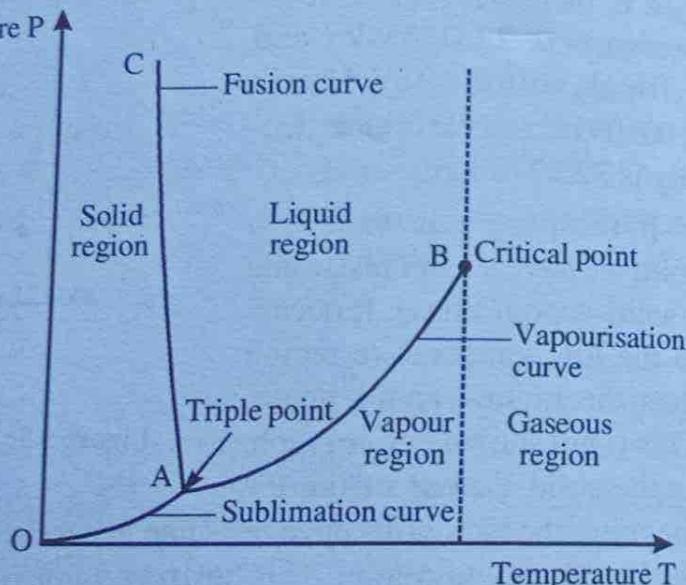


Figure 5.8

and vapour is bounded by absolute zero and the triple point (ii) The vapourisation curve on which vapour and liquid lie is bounded by the triple point and the critical point and (iii) solid and liquid lies on the fusion curve starts at the triple point and is unbounded.

In the case of water the sublimation curve is called the frost line, the vapourisation curve is called the steam line and the fusion line is called the ice line.

Distinction between PT and PV diagrams

1. In a PT diagram no two phase regions are shown but in a PV diagram two phase regions are shown. In PT diagram two phases collapse into one of the three curves.
2. The PT diagram gives the triple point where the sublimation, vapourisation and fusion curve meets. PV diagrams gives triple phase state line not triple point.

The essential feature of triple point is that **three phases, solid, liquid and vapour coexist in equilibrium. However a triple point is defined as the state in which two different solid phases coexist with a liquid or three different solid phases coexist.**

PT diagram enables us to distinguish between gas and vapour. Away from the curves there are only single phase equilibrium state. Above the critical temperature we can see a single phase equilibrium state called gas. So gas can be defined as follows. **A substance with no free surface and with a volume determined by that of the container when the temperature is above the critical temperature is called gas.**

Below the critical temperature gas in equilibrium with liquid is called vapour. The properties of vapour and gas are the same except that a vapour can be liquid by an isothermal increase of pressure due to compression but a gas cannot be liquefied no matter how high the pressure. There is an exemption, helium gas can be solidified under high pressure.

First order phase transitions: Calusius Clapeyron equation

Changes of phase

Almost all substances can exist in different forms such as solid, liquid and vapour. Each one is said to be a phase. When solid changes to liquid or liquid changes to vapour it is called as the phase change. Here we will see during changes of phase what happens to the thermodynamical variables P, T, V, S, U and G.

Let us consider the equilibrium between the liquid phases and its vapour phases of the same substance enclosed in a cylinder. The temperature and pressure are equal in both the phases. As each of these phases is in equilibrium, the temperature and

pressure must remain constant throughout the phase and hence the thermodynamical coordinates. V, S, U and G will be equal to the product of the specific value and mass of the substance in that phase.

Suppose m_1 and m_2 are the masses in the liquid and vapour phases and g_1 and g_2 are the specific values of the Gibbs potential in the two phases. Then for the whole system.

$$G = m_1 g_1 + m_2 g_2$$

If a small quantity of liquid changes into vapour, differentiating the above equation we get

$$\delta G = \delta m_1 g_1 + \delta m_2 g_2 \quad \dots \dots \text{ (i)}$$

Since the phase change occurs at constant temperature and pressure, the process is isothermal and isobaric.

$$\therefore \delta G = 0$$

\therefore Equation (i) becomes

$$0 = \delta m_1 g_1 + \delta m_2 g_2$$

$$\text{But} \quad \delta m_1 = -\delta m_2$$

$$g_1 = g_2$$

This shows that the thermodynamical Gibbs Potential per unit mass (g) will be equal in the two phases. This is valid for solid to liquid, liquid to vapour and vice versa.

First order phase transition

The changes of phase which takes place at constant temperature and pressure and in which heat is either absorbed or evolved are called first order phase transitions. In first order phase transitions, the entropy and density (or volume) change. The Gibbs function G remains constant in both phases, while its derivatives with respect to temperature and pressure is discontinuous at transition point.

Transformation of ice into water, water into vapour are examples of first order phase transition:

Now we will see whether a change in pressure will produce any effect on temperature on transition from one phase into the other. The answer will be given by Clausius - Clapeyron equation.

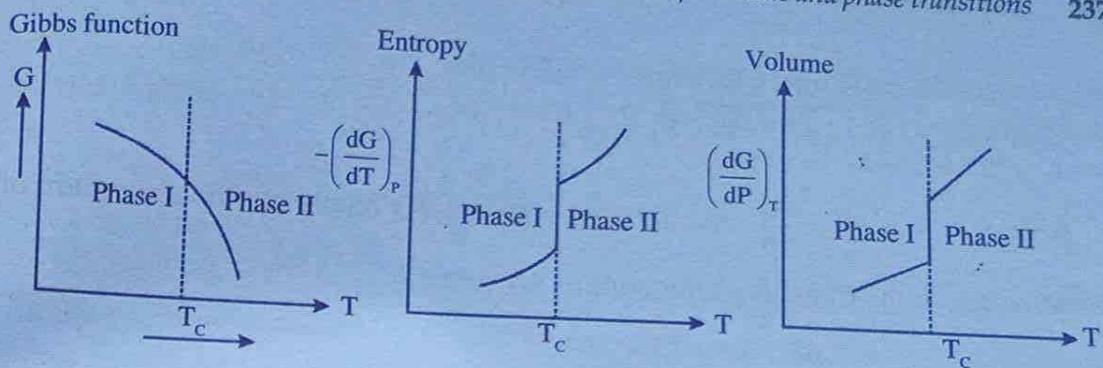


Figure 5.9: First order phase transition

Consider an enclosure containing a liquid and its saturated vapour in equilibrium. If this system undergoes an isothermal, isobaric change, we know that, the Gibb's potential of both phases are the same

$$\text{i.e., } G_1 = G_2$$

This is at pressure P and temperature T.

Let the temperature of the system be increased from T to $T + dT$ and pressure be increased from P to $P + dP$, then Gibb's potential goes from $G_1 + dG_1$ to $G_2 + dG_2$. So we must have

$$G_1 + dG_1 = G_2 + dG_2$$

or

$$dG_1 = dG_2 \quad (\because G_1 = G_2)$$

We have

$$G = U - TS + PV$$

Taking the differential on both sides we get

$$dG = dU - TdS - SdT + PdV + VdP$$

$$dU = TdS - PdV$$

$$dG = -SdT + VdP$$

$$dG_1 = -S_1dT + V_1dP$$

$$dG_2 = -S_2dT + V_2dP$$

Since

$$dG_1 = dG_2, \text{ we have}$$

$$-S_1dT + V_1dP = -S_2dT + V_2dP$$

$$(S_2 - S_1)dT = (V_2 - V_1)dP$$

$$\text{or } \frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1}$$

Now $S_2 - S_1 = dS = \frac{dQ}{T}$ and T being constant dQ represents the absorption of latent heat L at the transition temperature, we get

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

This is our Clausius - Clapeyron latent heat equation.

It is also very interesting to note the changes of specific heat capacity at constant pressure C_p , coefficient of cubical expansion β , and compressibility k during a first order phase change. All these parameters go to infinity. This is because transition occurs at constant T and P. When P is constant, $dT = 0$ or when T is constant, $dP = 0$

$$\therefore C_p = T \left(\frac{\partial S}{\partial T} \right)_p \rightarrow \infty$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow \infty$$

$$B = - \left(\frac{\partial P}{\partial V/V} \right)_T \rightarrow 0$$

$$k = \frac{1}{B} = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \rightarrow \infty$$

compressibility k is the reciprocal of bulk modulus B.

The Clausius - Clapeyron equation for 1 mole of substance becomes

$$\frac{dP}{dT} = \frac{s_2 - s_1}{(v_2 - v_1)}$$

where s_1 and s_2 are initial and final the molar entropies and v_2 and v_1 are final and initial molar volumes respectively.

Remember that $s_2 - s_1 = \frac{h_2 - h_1}{T}$

where s_1 and s_2 are initial and final molar entropies and h_1, h_2 are initial and final molar enthalpies.

Thus

$$\frac{dP}{dT} = \frac{h_2 - h_1}{T(v_2 - v_1)}$$

This is another form of Clausius-Clapeyron equation.

Clausius-Clapeyron equation and phase diagrams

The Clausius-Clapeyron equation plays an important role in the analysis of phase diagrams. In a phase diagram we found the sublimation curve, vapourisation curve and fusion curve. A point on each curve represents the coexistence of two phases except at the triple point and the critical point. Each point on the curve gives the thermodynamic coordinates P and T . But Clausius-Clapeyron equation is not concerned with coordinates rather it deals with the slope of the curve $\left(\frac{dP}{dT}\right)$.

Here we analyse the phase diagram for water in the light of Clausius-Clapeyron equation.

Consider a sample of ice at temperature T (which is less than its melting point) opened to atmospheric pressure P . The system is in its solid state and is represented by a point 'a' on the phase diagram shown in figure below.

Suppose heat is given to the system, its temperature increases so also its enthalpy. During this the state of the system moves horizontally until it reaches the fusion curve. Absorption of heat melts ice produce water. After reaching the fusion curve the system again absorbs heat without any change of temperature. The corresponding temperature is called normal melting point represented by

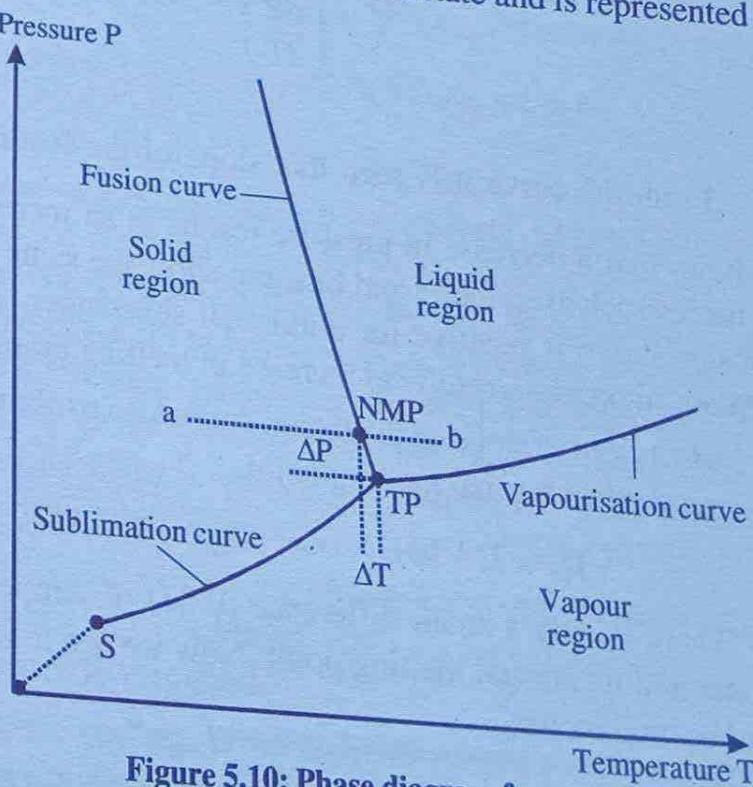


Figure 5.10: Phase diagram for water

a point NMP on the fusion curve. When ice melts completely the temperature of the system rises again. This is represented by a horizontal line (pressure constant) move along to the point b. The point b is in the liquid region. Supplying heat again the line moves towards the vapourisation curve.

Now we change the scenario. Suppose our system is at NMP, where ice coexists with water and air at standard atmospheric pressure. If the sample is placed in a chamber and the air pressure of the system is lowered. It is due to small decrease in pressure (say ΔP), the system is no longer on the fusion curve. The result is that the temperature of the system will change by ΔT to return to the fusion curve.

From the graph we get

$$\frac{\Delta P}{\Delta T} = \tan \theta$$

where $\tan \theta$ is the slope of the fusion curve $\frac{dP}{dT}$ approximately.

i.e.

$$\frac{\Delta P}{\Delta T} = \frac{dP}{dT}$$

or

$$\Delta T = \frac{\Delta P}{\left(\frac{dP}{dT} \right)}$$

From the curve it is seen that slope of the fusion curve $\frac{dP}{dT}$ is negative. This shows that a decrease in pressure results in an increase in the melting point. Substances such as graphite and bismuth show the same behaviour. In general slope of fusion curve is positive for almost all substances. Positive slope implies that increase in pressure results in increase in melting point and vice versa.

The negative slope of the fusion curve also explains why the triple point of water is greater than normal melting point.

$$T_{TP} = 273.16 \text{ K} \quad \text{and} \quad T_{NMP} = 273.15 \text{ K}.$$

There is only a small difference (0.01) of temperature between triple point of water and its normal melting point. Now we are in a position to define triple point and normal melting.

Definitions of TP and NMP point of water using phase diagram

Triple point: It is the temperature at which ice and water are in equilibrium with water vapour with a vapour pressure of 612 Pa.

Normal melting point: It is the temperature at which ice and water are in equilibrium with air at a standard atmospheric pressure.

Now we will see how to arrive at difference in value of temperature between T_{TP} and T_{NMP} using Clausius-Clapeyron equation.

We have

$$\Delta T = \frac{\Delta P}{\left(\frac{dP}{dT}\right)}$$

Substituting for $\frac{dP}{dT}$ from Clausius-Clapeyron equation, we get

$$\Delta T = \frac{T(v_2 - v_1)}{(h_2 - h_1)} \Delta P$$

The subscript 1 refers to the solid phase and 2 refers to the liquid phase. Putting the values for all parameters

$$T = 273 \text{ K}, v_1 = 19.65 \times 10^{-6} \text{ m}^3 / \text{mol}, v_2 = 18.02 \times 10^{-6} \text{ m}^3 / \text{mol},$$

$$h_2 - h_1 = 6.01 \times 10^3 \text{ J mol}^{-1} \text{ and } \Delta P = 1.01 \times 10^5 \text{ Pa, we get}$$

$$\Delta T = -0.0073 \text{ K.}$$

That is, the increase of pressure depresses the temperature from the triple point of ice by 0.0073 K. The lowering of temperature from the triple point of ice to the normal melting point is also affected by the air that is dissolved in a mixture of ice and water. The effect of the dissolved air is to lower the temperature at which ice melts by 0.0023 K with respect to melting temperature of pure water. Therefore, the two effects combine to lower the temperature of the triple point by 0.0096 K or approximately 0.01 K. The triple point is arbitrarily assigned an exact value of 273.16 K, the result is that the normal melting point is approximately 273.15 K.

The above discussion can be used to explain the phenomenon of regelation. **Regelation is defined as the phenomenon in which ice melts under high pressure and freezes again when this pressure is removed.**

This is the principle behind ice skating. When a person stands on a skating platform, it is due to the pressure exerted by the person the melting point of ice under the

skating blade decreases and ice melts. This provides a slippery (water) surface to move the skate.

Unlike fusion curves the slope of sublimation and vapourisation curves of all substances is always positive, because the molar volume of vapour is always larger than the molar volume of liquid. This increase in volume suggests that the vapour has more disorder than its solid or liquid that change in entropy $s_2 - s_1$ is positive.

$$\text{We have } \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

$s_2 - s_1$ is positive and $v_2 - v_1$ is positive implies that $\frac{dP}{dT}$ is positive. This means that when pressure increases the boiling point also increases and vice versa.

Example 16

Calculate the melting point of ice under a pressure of 2 atmospheres. It is given that the melting point of ice under one atmospheric pressure is 273.16 K. Latent heat of fusion of ice is 79.6 cal/g and at the melting point specific volume of ice is 1.0908 cc and that of water is 1.0001 cc. One atm = 1.013×10^6 dynes cm⁻².

Solution

$$L = 79.6 \times 4.185 \text{ ergs g}^{-1}$$

$$T = 273.16 \text{ K}$$

$$V_2 = 1.0001 \text{ cc}$$

$$V_1 = 1.0908 \text{ cc}$$

$$dP = 2 - 1 = 1 \text{ atm} = 1.013 \times 10^6$$

Using

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$\frac{dT}{dP} = \frac{dPT(V_2 - V_1)}{L}$$

$$= \frac{1.013 \times 10^6 \times 273.16 \times (1.0001 - 1.0908)}{79.6 \times 4.185 \times 10^7}$$

$$= -0.007533 \text{ K}$$

∴ The new melting point is $273.16 - 0.007533 = 272.41\text{ K}$

Example 17

Calculate the boiling point of water under a pressure of two atmospheres. It is given that the boiling point of water under a pressure of one atmosphere is 373.2K. Latent heat of vapourisation is 539 cal/g. Specific volume of water is 1cc and specific volume of steam is 1674 cc.

Solution

$$dP = 2 - 1 = 1 \text{ atm} = 1.013 \times 10^6 \text{ dynes cm}^{-2}$$

$$V_2 = 1674 \text{ cc}$$

$$V_1 = 1 \text{ cc}$$

$$L = 539 \times 4.185 \times 10^7 \text{ erg/g}$$

$$T = 373.2 \text{ K}$$

Using

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

or

$$dT = \frac{dP \cdot T \cdot (V_2 - V_1)}{L}$$

$$= \frac{1.013 \times 10^6 \times 373.2 \times (1674 - 1)}{539 \times 4.185 \times 10^7}$$

$$dT = 28.04 \text{ K.}$$

$$\therefore \text{Boiling point} = 373.2 + 28.04 = 401.24 \text{ K}$$

Example 18

Calculate under what pressure ice freezes at 272 K if the change in specific volume when 1 kg of water freezes is $91 \times 10^{-6} \text{ m}^3$. Latent heat of ice $3.36 \times 10^5 \text{ J kg}^{-1}$

$$dT = 273 - 272 = 1 \text{ K}$$

$$V_2 - V_1 = 91 \times 10^{-6} \text{ m}^3$$

$$T = 273$$

$$L = 3.36 \times 10^5 \text{ J kg}^{-1}$$

Using

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$\begin{aligned} dP &= \frac{LdT}{T(V_2 - V_1)} = \frac{3.36 \times 10^5 \times 1}{273 \times 91 \times 10^{-6}} \\ &= 13.525 \times 10^6 \text{ Nm}^{-2} \\ \text{or } dP &= \frac{13.525 \times 10^6}{1.013 \times 10^5} = 133.5 \text{ atm} \end{aligned}$$

Example 19

Calculate the change in temperature of boiling water when the pressure is increased by 2.712 cm of Hg. The normal boiling point of water at atmospheric pressure is 100°C. Latent heat of steam is 537 cal g⁻¹ and specific volume of steam 1674 cc.

Solution

$$\begin{aligned} dP &= 2.712 \text{ cm of Hg} \\ &= 2.712 \times 13.6 \times 980 \text{ dynes cm}^{-2} \end{aligned}$$

$$T = 100 + 273 = 373$$

$$V_1 = 1 \text{ cc}, \quad V_2 = 1674 \text{ cc}, \quad L = 537 \times 4.2 \times 10^7 \text{ ergs}$$

Using

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \cdot T \cdot (V_2 - V_1)}{L}$$

$$dT = \frac{2.712 \times 13.6 \times 980 \times 373 \times (1674 - 1)}{537 \times 4.2 \times 10^7}$$

$$dT = 1 \text{ K.}$$

Example 20

The latent heat of fusion of ice I is $3.34 \times 10^5 \text{ J kg}^{-1}$ at 0°C and atmospheric pressure. If the change in specific volume on melting is $-9.05 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$, then calculate the change of melting temperature due to change of pressure.

Solution

$$L = 3.34 \times 10^5 \text{ J kg}^{-1}, T = 273 \text{ K}, v_2 - v_1 = -9.05 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$$

Using

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}$$

or

$$dT = \frac{T(v_2 - v_1)}{L} dP$$

$$dT = \frac{-273 \times 9.05 \times 10^{-5}}{3.34 \times 10^5} dP$$

$$dT = 7.39 \times 10^{-8} dP$$

If $dP = 1 \text{ atm}$

$$\therefore \text{change melting temperature} = 7.39 \times 10^{-8} \text{ K Pa}^{-1}$$

IMPORTANT FORMULAE

1. Legendre transformation:

If f is a function of (x, y) , then $g(u, y)$ is

$$g(u, y) = f - ux$$

where

$$u = \frac{\partial f}{\partial x}$$

2. Enthalpy (H):

$$H = H(V, S)$$

$$H = U + PV$$

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T, \quad \left(\frac{\partial H}{\partial P} \right)_S = V$$

3. Helmholtz function (A):

$$A = A(S, V)$$

$$A = U - TS$$

$$dA = -PdV - SdT$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P, \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

4. Gibb's function (G):

$$G = G(P, T)$$

$$G = A + PV$$

or

$$G = U - TS + PV$$

or

$$G = H - TS$$

$$dG = VdP - SdT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

5. Internal energy function (U):

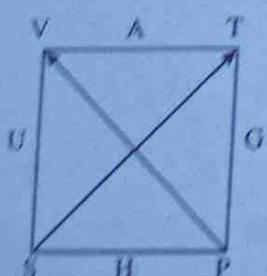
$$U = U(V, S)$$

$$dU = -PdV + TdS$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P, \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

$$6. \quad C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V; \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

7. VAT - VUS diagram:



8. Condition for exact differential:

$$\left(\frac{\partial M}{\partial y}\right)_z = \left(\frac{\partial N}{\partial x}\right)_y.$$

9. Maxwell's relations:

$$(i) \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$(ii) \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$(iii) \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$(iv) \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

10. (i) First TdS equation: $S(T, V)$

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

(ii) Second TdS equation: $S(T, P)$

$$TdS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

(iii) third TdS equation: $S = S(P, V)$

$$TdS = C_V \left(\frac{\partial T}{\partial P} \right)_V dP + C_P \left(\frac{\partial T}{\partial V} \right)_P dV.$$

11. For a perfect gas:

$$\left(\frac{\partial U}{\partial T} \right)_V = 0$$

12. For a real gas:

$$U = \int C_V dT - \frac{a}{V} + \text{constant}$$

13. Volume expansivity:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

14. Isothermal compressibility: $k = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

15. When a system undergoes a reversible isothermal change of pressure

(i) Heat transferred

$$Q = -TV\beta(P_f - P_i)$$

(ii) Work done $W = \frac{kV}{2} (P_f^2 - P_i^2)$

(iii) Change in internal energy

$$\Delta U = Q + W.$$

16. When a system undergoes a reversible adiabatic change of pressure

change in temperature $\Delta T = \frac{TV\beta}{C_p} (P_f - P_i).$

17. For a first order phase change

- (i) Pressure and temperature are constant
(ii) Gibb's free energy is continuous

$$G_1 = G_2$$

(iii) The entropy and density (volume) change.

18. Clausius' Clapeyron equation:

(i) $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$

(ii) $\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$

(iii) $\frac{dP}{dT} = \frac{h_2 - h_1}{T(v_2 - v_1)}$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in about two or three sentences)

Short answer type questions

1. What is Legendre transformation?
2. What are thermodynamic functions?
3. What are thermodynamic potentials?
4. Define internal energy of a system. What are its properties?
5. What is Helmholtz free energy? Give two of its properties.
6. What is enthalpy? Give two of its properties.
7. What is Gibbs function? Give two of its properties.
8. How will you construct enthalpy H from internal energy U?

9. What is the significance of thermodynamic potential?
10. What is throttling process?
11. What is the connection between throttling process and enthalpy?
12. Why do we say that dU , dF , dH and dG are exact differentials?
13. Write down the four Maxwell's relationships.
14. Write down the Clapeyron latent heat equation, and explain the symbols.
15. Explain the effect of change of pressure on the melting point.
16. Explain the effect of change of pressure on the boiling point.
17. Write down TdS equations and explain the symbols.
18. What is phase change?
19. Define a first order phase change. Give two examples.
20. How will you characterise a first order phase change?
21. Draw the graphical variation of Gibb's potential, entropy and volume with respect to temperature during a first order phase change.
22. What is the effect of change in pressure on temperature during first order phase transition?
23. What is meant by a pure substance?
24. What is a phase diagram?
25. Draw a PV diagram for a pure substance.
26. Draw phase diagram for pure water.
27. Distinguish between gas and vapour.
28. Draw the density curve of liquid and vapour.
29. Distinguish between PT and PV diagrams.
30. Define the following:
 - (i) sublimation curve (ii) vapourisation curve and (iii) fusion curve.
31. What is triple point?
32. Distinguish between triple point and normal melting point of ice.
33. What is regelation?
34. What is the relation between Clausius-Clapeyron equation and phase diagram?
35. During first order phase what happens to the parameters C_p , β and K .

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type questions

1. Starting from internal energy U , derive the remaining thermodynamic functions using Legendre transformation.

2. Distinguish between $-\int PdV$ and $\int VdP$.
3. Derive the condition for exact differential.
4. Derive any two Maxwell's relations.
5. Derive the first TdS equation.
6. Derive the second TdS equation.
7. Derive the third TdS equation.
8. Derive the relation $\left(\frac{\partial U}{\partial S}\right)_V = T$
9. Derive the relation $\left(\frac{\partial H}{\partial S}\right)_P = T$
10. Derive the relation $\left(\frac{\partial U}{\partial V}\right)_S = -P$
11. Derive the relation $\left(\frac{\partial H}{\partial P}\right)_S = V$
12. Derive the relation $\left(\frac{\partial H}{\partial T}\right)_P = C_P$.
13. Using Maxwell's equation show that for a Vander waal's gas $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$
14. Using Maxwell's relation show that $\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$
15. Prove that $\left(\frac{\partial C_P}{\partial P}\right)_T = 0$ for all gases.
16. Water boils at a temperature of 101°C at a pressure of 787 mm of Hg. One gram of water occupies 1601cm^3 on evaporation. Calculate the latent heat of vapourisation. [511.33 cal/g]
17. Calculate the change in the melting point of ice when it is subjected to a pressure of 100 atmospheres
Density of ice = 0.917 gcm^{-3} and latent heat of ice = 336 Jg^{-1} . [-0.7326 K]
18. Lead is melted at 600K at one atmospheric pressure. Its density decreases from 11.01 to

10.65 g cm^{-3} . The latent heat of fusion is 24.5 J g^{-1} . What is the melting point at a pressure of 100 atmospheres.

19. The ratio of densities of ice and water at 0°C is $\frac{10}{11}$. Calculate the decrease in the melting point of ice. $L = 80 \text{ cal g}^{-1}$ and change in specific volume 0.1 cc g^{-1} . The increase in pressure is one atmosphere. [$8.2 \times 10^{-3} \text{ K}$]
20. Calculate the change in melting point of naphthalene for 2 atmosphere rise in pressure. Melting point of naphthalene is 80°C . $L = 4563 \text{ cal/mol}$. Increase in volume on fusion $18.7 \text{ cm}^3 \text{ mol}^{-1}$. [0.06976 K]
21. Show that for an ideal gas $A = \int C_v dT - T \int \frac{C_v}{T} dT - nRTV - \text{constant } T + \text{constant}$
22. Derive the relation $H = G - T \left(\frac{\partial G}{\partial T} \right)_P = -T^2 \left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_P$.
23. Derive the relation $C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P$.
24. Show that the Legendre transformation $J \left(\frac{1}{T}, V \right)$ that produces the thermodynamical potential $Y \left(\frac{1}{P}, \frac{P}{T} \right)$ known as the Planck function and defined by the transformation
- $$Y = -\frac{H}{T} + S = -\frac{G}{T}$$
- and
- $$dY = \frac{H}{T^2} dT - \frac{V}{T} dP$$
- where
- $$J = -\frac{U}{T} + S$$
25. From the fact that $\frac{dV}{V}$ is an exact differential, derive the relation

$$\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial k}{\partial T}\right)_P.$$

26. Show that the second TdS equation may be written as

$$TdS = C_p dT - V\beta TdP.$$

27. The pressure on 0.2 kg of water is increased reversibly and isothermally from atmospheric pressure to 3×10^8 Pa at 20°C. $\beta = 206.80 \times 10^{-6} \text{ K}^{-1}$, $k = 4.589 \times 10^{-10} \text{ Pa}^{-1}$

- a) How much heat is transferred
- b) How much is the work done
- c) Calculate the change in internal energy.

28. Derive the relation $\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$.

29. A gas obeys the equation $P(v - b) = RT$ where b is constant and c_v is constant show that $P(v - b)^\gamma = \text{constant}$ for an adiabatic process.

30. When lead is melted at atmospheric pressure, the melting point is 600 K, the density decreases from 11.01 to 10.65 g cm⁻³ and latent heat of fusion is 24.5 J g⁻¹. What is the melting point at the pressure of 1.01×10^7 Pa ? [600.76 K]

Section C

(Answer questions in about two pages)

Long answer type questions (Essays)

1. Derive Maxwell's four thermodynamical relations. Use one of them to obtain Clausius - Clapeyron's latent heat equation.
2. Deduce thermodynamic potentials and derive Maxwell's relations.
3. Discuss the first order phase transition in detail.
4. Discuss the second order phase transition in detail.
5. Discuss the phase diagram for pure water in detail.

Hints to problems

1 to 12 - All book works

13. See example 1

We have $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ (1)

For Vander waal's gas $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

Find $\left(\frac{\partial P}{\partial T}\right)_V$ and substitute in eq (1).

14. Start with $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ then proceed as in example 3

Remember that $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

15. See example 13.

$$16. \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 787 - 760 = 27 \text{ mm of Hg}$$

$$dT = 1\text{K}, V_2 - V_1 = 1601 - 1 = 1600, T = 373\text{K}$$

$$17. \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 100 - 1 = 99 \text{ atm} = 99 \times 76 \times 13.6 \times 980$$

$$L = 336 \times 10^7 \text{ ergs g}^{-1} \quad T = 273\text{K}$$

$$V_2 - V_1 = 1 - \frac{1}{0.917} = -0.091 \text{ cm}^3 \quad \text{Find } dT.$$

$$18. \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 100 - 1 = 99$$

$$= 99 \times 76 \times 13.6 \times 980$$

$$L = 24.5 \text{ J/g} = 24.5 \times 10^7 \text{ ergs g}^{-1} \quad V_1 = \frac{1}{11.01} \text{ cm}^3, \quad V_2 = \frac{1}{10.65} \text{ cm}^3 \quad \text{Find } dT.$$

$$19. dP = 1.01 \times 10^5 \text{ Nm}^{-2} \quad L = 80 \times 4.2 \times 10^3 \text{ J kg}^{-1}$$

$$T = 273\text{K} \quad V_2 - V_1 = -0.1 \text{ cm}^3 \text{ g}^{-1} = -0.1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \quad \text{Find } dT$$

$$20. dP = 2 \text{ atm} = 2 \times 1.013 \times 10^6 \text{ dynes cm}^{-2}$$

$$T = 80 + 273 \quad L = 4563 \times 4.2 \times 10^7 \text{ ergs mol}^{-1}$$

$$V_2 - V_1 = 18.7 \text{ cm}^3 \quad \text{Find } dT.$$

21. We have

For ideal gas

$$dA = -SdT - PdV \quad \dots\dots (1)$$

$$PV = nRT$$

$$\therefore dA = -SdT - \frac{nRT}{V}dV \quad \dots\dots (2)$$

Use

$$S = \int \frac{dQ}{T}$$

Then integrate eqn (2) to get the result.

22. We have

$$G = H - TS$$

or

$$H = G + TS \quad \dots\dots (1)$$

But

$$dG = VdP - SdT$$

$$\therefore \left(\frac{\partial G}{\partial T} \right)_P = -S. \text{ Put this in eq (1)}$$

$$H = G - \left(\frac{\partial G}{\partial T} \right)_P$$

The above relation can be written as

$$H = T^2 \left[G - \frac{T \left(\frac{\partial G}{\partial T} \right)_P}{T^2} \right]$$

$$\text{but} \quad \frac{T \left(\frac{\partial G}{\partial T} \right)_P - G}{T^2} = \frac{\partial}{\partial T} (G/T)$$

$$\therefore H = -T^2 \frac{\partial}{\partial T} (G/T)$$

23. We have

$$H = G + TS$$

Differentiate with respect to T, keeping P constant

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial G}{\partial T} \right)_P + T \left(\frac{\partial S}{\partial T} \right)_P + S$$

or

Use

$$C_p = \left(\frac{\partial G}{\partial T} \right)_p + T \left(\frac{\partial S}{\partial T} \right)_p + S$$

$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad \text{and we get} \quad -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

24. $f(x, y) \rightarrow g(u, y)$ $g = f - ux$

Here $J\left(\frac{1}{T}, V\right) \rightarrow Y\left(\frac{1}{T}, \frac{P}{T}\right)$

we get $Y = J\left(\frac{1}{T}, V\right) - \frac{PV}{T}$

$$Y = -\frac{U}{T} + S - \frac{PV}{T}$$

$$Y = -\frac{U + TS}{T} - \frac{PV}{T}$$

..... (2)

Use $H = U - TS$ $Y = -\frac{H}{T} + S$

Taking the differential of eq (2), we get

$$dY = \frac{H}{T^2} dT - \frac{V}{T} dP.$$

25. Since $\frac{dV}{V}$ is an exact differential we can write

$$\left(\frac{\partial^2 V}{\partial T \partial P} \right)_P = \left(\frac{\partial^2 V}{\partial P \partial T} \right)_T$$

Using

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

The above eqn becomes

$$\left[\frac{\partial}{\partial T} (-kV) \right]_P = \left[\frac{\partial}{\partial P} (\beta V) \right]_T$$

Perform differentiation

$$-k \left(\frac{\partial V}{\partial T} \right)_P - V \left(\frac{\partial \kappa}{\partial T} \right)_P = \beta \left(\frac{\partial V}{\partial P} \right)_T + V \left(\frac{\partial \beta}{\partial P} \right)_T$$

Divide by V

$$-\frac{k}{V} \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial \kappa}{\partial T} \right)_P = \frac{\beta}{V} \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial \beta}{\partial P} \right)_T$$

or

$$-\frac{k}{V} \left(\frac{\partial V}{\partial T} \right)_P - \frac{\beta}{V} \left(\frac{\partial V}{\partial P} \right)_T = \left(\frac{\partial \kappa}{\partial T} \right)_P + \left(\frac{\partial \beta}{\partial P} \right)_T$$

Substituting for

$$\left(\frac{\partial V}{\partial T} \right)_P = \beta V$$

and

$$\left(\frac{\partial V}{\partial P} \right)_T = -kV$$

$$-\frac{k}{V} \cdot \beta V - \frac{\beta}{V} - kV = \left(\frac{\partial \kappa}{\partial T} \right)_P + \left(\frac{\partial \beta}{\partial P} \right)_T$$

$$0 = \left(\frac{\partial \kappa}{\partial T} \right)_P + \left(\frac{\partial \beta}{\partial P} \right)_T$$

or

$$\left(\frac{\partial \beta}{\partial P} \right)_T = - \left(\frac{\partial \kappa}{\partial T} \right)_P$$

26. From second TdS equation, we have

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP.$$

Using

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \beta V$$

$$TdS = C_p dT - T \beta V dP.$$

27. a) Heat transferred

$$Q = -T\beta V(P_f - P_i)$$

$$T = 20 + 273 = 293 \text{ K}$$

$$V = \frac{m}{\rho} = \frac{0.2}{10^3}$$

$$\beta = 206.80 \times 10^{-6} \text{ K}^{-1}$$

$$P_f - P_i = (3 \times 10^8 - 1 \times 10^5) = 2999 \times 10^5$$

$$Q = -3634.3 \text{ J}$$

Substituting

b) Work done

$$= \frac{kV}{2} (P_f^2 - P_i^2)$$

$$= \frac{4.589}{2} \times 10^{-10} \times 0.2 \times 10^{-3} [(3 \times 10^8)^2 - (10^5)^2]$$

$$= 4130.1 \text{ J}$$

c) Change in internal energy

$$\Delta U = Q + W = 495.8 \text{ J}$$

28. From Maxwell's relations

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

Differentiate with respect to temperature

$$\left(\frac{\partial^2 S}{\partial T \partial P} \right)_T = - \left(\frac{\partial^2 V}{\partial T^2} \right)_P \quad \dots \dots (2)$$

But $C_P = T \left(\frac{\partial S}{\partial T} \right)_P$, we get

$$\left(\frac{\partial C_P}{\partial P} \right)_T = T \left(\frac{\partial^2 S}{\partial T \partial P} \right)_T \quad \dots \dots (4)$$

From eqs 2 and 4 we get the result.

29. We have

$$dQ = dU + PdV$$

$$TdS = C_V dT + PdV$$

For adiabatic process $dS = 0$ and put $P = \frac{RT}{V - b}$

$$0 = C_v dT + \frac{RT}{v-b} dv$$

Using

$$C_p - C_v = nR$$

$$c_p - c_v = R$$

$$c_v \frac{dT}{T} + (c_p - c_v) \frac{T}{v-b} dv = 0$$

Divide by T

$$c_v \frac{dT}{T} + (c_p - c_v) \frac{dv}{v-b}$$

Integrate

$$c_v \ln T + (c_p - c_v) \ln(v-b) = \text{constant}$$

Divide by c_v

$$\ln T + (\gamma - 1) \ln(v-b) = \text{constant}$$

$$\ln T - \ln(v-b) + \gamma \ln(v-b) = \text{constant}$$

$$\ln \frac{T}{v-b} + \ln(v-b)^\gamma = \text{constant}$$

$$\ln \frac{P}{R} + \ln(v-b)^\gamma = \text{constant}$$

$$\ln \frac{P(v-b)^\gamma}{R} = \text{constant}$$

or

$$P(v-b)^\gamma = \text{constant}$$

30. Use $\frac{dP}{dT} = \frac{l}{T(v_1 - v_2)}$

$$dT = \frac{T(v_1 - v_2)}{l} dP.$$

$$T = 600 \text{ K}, v_1 - v_2 = \frac{1}{\rho_1} - \frac{1}{\rho_2}, l = 24.5 \text{ J g}^{-1}, dP = 1.01 \times 10^7 - 1.01 \times 10^5,$$

we get 600.75 K.